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## Nuclear Forensic Analysis of an Unknown Uranium Ore Concentrate Sample Seized in a Criminal Investigation in Australia

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### Abstract

Early in 2009, a state policing agency raided a clandestine drug laboratory in a suburb of a major city in Australia. During the search of the laboratory, a small glass jar labelled “Gamma Source” and containing a green powder was discovered. The powder was radioactive. This paper documents the detailed nuclear forensic analysis undertaken to characterise and identify the material and determine its provenance. Isotopic and impurity content, phase composition, microstructure and other characteristics were measured on the seized sample and the results were compared with similar material obtained from the suspected source (ore and ore concentrate material). While an extensive range of parameters were measured, the key ‘nuclear forensic signatures’ used to identify the material were the U isotopic composition, Pb and Sr isotope ratios, and the rare earth element pattern. These measurements, in combination with statistical analysis of the elemental and isotopic content of the material against a database of uranium ore concentrates sourced from mines located worldwide, led to the conclusion that the seized material (a uranium ore concentrate of natural isotopic abundance) most likely originated from Mary Kathleen, a former Australian uranium mine.

**Keywords:** Nuclear forensics; uranium ore concentrate; nuclear forensic signatures

### Introduction

In May 2009, officers from a state policing agency in Australia requested that the Australian Nuclear Science and Technology Organisation (ANSTO) provide identification and provenance of an unknown radioactive powder sample seized in a raid on a clandestine drug laboratory. The sample was found and transported to ANSTO in a small glass jar (Figure 1). No radioactive contamination was detected on the outside of the jar.

The analytical sequence initiated by ANSTO generally followed that proposed by the International Atomic Energy Agency’s (IAEA) model action plan (MAP) [1, 2]. For this investigation, mostly comparative signatures were used; that is, comparisons were made between the material characteristics of the seized sample and those same characteristics for samples of known origin. In this way, analytical data were interpreted to provide information to the state police on the material’s identification and provenance. Previous research has been conducted by ANSTO and others into the assessment of various signatures for origin determination of uranium ore concentrates (UOC). Particularly valuable measurements for attributing UOCs have included isotopic ratios of Sr, Nd, and Pb, the level of elemental and

anionic impurities, and the pattern of rare earth element concentrations [3-7]. Lawrence Livermore National Laboratory (LLNL) has been working in this field for some time and has developed an extensive database of analytical measurements on UOC samples from around the globe (as well as an archive of physical samples) with which to compare unknown UOC samples. They have developed the Discriminant Analysis Verification Engine (DAVE) algorithm, based upon the iterative application of partial least squares discriminant analysis (PLS-DA), designed to assist matching of the characteristics of an unknown UOC with signatures contained in the database [8-10]. A sub-sample of the seized material was sent to LLNL for comparison against the uranium sourcing database using DAVE, confirmation of the analytical results obtained at ANSTO, and additional characterisation of the material as required.

## **Materials and Methods**

### **Materials**

An unknown radioactive powder sample was provided to ANSTO by an Australian state policing agency. It was given the identification NSR-F-130509, which is used throughout this paper. The sample was contained in a small, clear glass jar with a metal screw-top lid (Figure 1), identical to a Kraft Vegemite™ jar. The glass jar contained 41.95 g of what appeared to be a free flowing, green granular powder (Figure 2). The material appeared to be homogeneous, with no visible indications of other materials or impurities. After initial analysis at ANSTO, a 10 g aliquot of this material was sent to LLNL.

Preliminary elemental analysis of the seized sample indicated that the rare earth element (REE) pattern was a close match to a previously analysed UOC sample sourced from Mary Kathleen. Therefore, a uranium ore and a UOC sample from Mary Kathleen Uranium mine were also characterised using some of the described techniques. The UOC (which was black in colour) was believed to have been produced in 1977, while the ore sample was mined in late 1980.

### **Characterisation techniques**

A summary of characterisation techniques used to examine the seized material is provided in Table 1. High resolution gamma-ray spectrometry (HRGS) measurements were conducted for initial ‘categorization’ of the seized sample (i.e. to provide insight into the nature of the material and identify risks to health and safety). HRGS was performed on the ‘as-received’ sample at ANSTO using a Canberra instrument with an HPGe detector. The acquisition period was 12 hours and the resulting spectrum was analysed using the ‘multi-group analysis for uranium (MGAU)’ software (version 3.0) to determine the approximate uranium isotopic abundance. LLNL performed gamma spectrometry using in-house HPGe gamma spectrometers. Spectra were acquired for 8 hours for initial categorization and then 3 days for confirmation. All spectra were analysed using an in-house version of the GAMANAL software.

Physical examination of the samples was conducted using both optical and electron microscopy. At ANSTO, the microstructure of NSR-F-130509 was characterised using scanning electron microscopy (SEM, JEOL JSM 6300), while elemental composition was measured using energy dispersive X-ray spectroscopy (EDS, Noran Instruments Voyager Series IV X-ray microanalysis system). At LLNL, the seized powder and an exemplar of



UOC produced at the Mary Kathleen uranium mine were analysed using an FEI Inspect F SEM/EDS. LLNL prepared the materials for SEM/EDS analysis by one of two methods: surface transfer of the as-received sample or ultrasonication in solvent to promote disaggregation of the material.

The phase composition of the samples was measured using X-ray diffraction (XRD). ANSTO used a Siemens Kristalloflex D500 spectrometer in conjunction with the X'Pert HighScore Pro™ package from Panalytical. LLNL used a Bruker D8 Discover MR XRD and Bruker software. X-ray fluorescence (XRF) was used to determine major elemental content (i.e., elements greater than approximately 0.05 wt %) [11]. ANSTO analysed pressed powders of NSR-F-130509 using a Philips PW2400 wavelength dispersive XRF. XRF was performed at LLNL on the as-received powders using a Bruker AXS S8 Tiger.

Total uranium content and the uranium isotopic composition were measured on the samples at LLNL using mass spectrometry. Sub-samples of NSR-F-130509 and the Mary Kathleen UOC exemplar were dissolved in HNO<sub>3</sub>/HF. Gravimetric dilutions of the resulting solutions were spiked with <sup>233</sup>U, purified using UTEVA (Eichrom Technologies) resin and analysed by high-resolution multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS, Nu Plasma) for total uranium content (by isotope dilution mass spectrometry (IDMS)) and uranium isotopic content.

Age-dating was performed at LLNL using the <sup>234</sup>U/<sup>230</sup>Th chronometer. Dissolutions of both NSR-F-130509 and the Mary Kathleen UOC exemplar were spiked with <sup>233</sup>U and <sup>229</sup>Th. Uranium and Th were then radiochemically separated, purified, and measured by MC-ICPMS (Nu Plasma). The concentrations of <sup>230</sup>Th relative to <sup>234</sup>U were used to calculate model ages [12], based upon the assumption that all Th was removed from the sample during processing and that the material remained a closed system afterwards (no loss or addition of Th). <sup>228</sup>Th was measured (at LLNL) using alpha spectrometry for the <sup>228</sup>Th/<sup>232</sup>Th isotope chronometer [13].

Isotopic ratios of Sr and Pb were analysed in NSR-F-130509 and the Mary Kathleen UOC exemplar at LLNL. Radiochemical separation of Sr and Pb was achieved using anion exchange column chromatography. The Sr fraction was purified using Sr-spec resin (Eichrom Technologies) and analysed by thermal ionization mass spectrometry (TIMS, ThermoFisher Triton); results were corrected for mass bias (instrument fractionation) using <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194. The Pb fraction was purified using AG1-X8 resin (Bio-Rad Laboratories) and analysed using MC-ICP-MS (Nu-Plasma). Pb isotopic results were corrected for mass bias using Tl added to the sample immediately prior to mass spectrometry analysis, using a <sup>205</sup>Tl/<sup>203</sup>Tl value of 2.3875.

Both laboratories analysed NSR-F-130509 for trace elemental impurities using quadrupole ICP-MS (Perkin Elmer Elan6000 at ANSTO and Thermo-Elemental X7 at LLNL). Acid digestions of the powder sample (~0.1 g) were diluted in a HNO<sub>3</sub>/HF solution to U concentrations of ~180 ppm; Rh internal standard was added. The Mary Kathleen UOC exemplar and the Mary Kathleen ore sample were analysed in the same manner at LLNL and ANSTO, respectively. ANSTO also measured the rare earth element content of the Mary Kathleen ore sample by neutron activation analysis (NAA), and found that where the elemental concentration was above detection limits for this technique, agreement with ICP-MS and XRF results was generally within about 5%. Note that NAA was not suitable for analysis of the ore concentrate samples as the high uranium content, which produces many

fission products when irradiated with thermal neutrons, interferes with the analysis. Anion analysis ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $PO_4^{3-}$ ) was conducted on the aqueous leachate of NSR-F-130509 and the Mary Kathleen UOC exemplar. The detailed procedure is described elsewhere [4].

### Statistical Analysis using Uranium Sourcing Database

LLNL has developed a 'Uranium Sourcing Database' (sponsored by U.S. Department of Energy/NA-243), which was used as a source of comparative signatures for this study. The database contains the results of over 6000 individual sample analyses (principally for elemental and isotopic content), representing material from over 130 production locations in approximately 30 countries. However, since the database includes sample analyses performed by different laboratories and for different purposes, not every sample analysis includes measurement of all parameters (elements and isotopes). Comparisons of the material characteristics of NSF-F-130509 to those of samples contained in the database were performed using both principal components analysis (PCA) and partial least squares-discriminant analysis (PLS-DA) in an attempt to determine the closest match between the material characteristics of the seized material and those of known specific production locations. Since both PCA and PLS-DA only operate on complete matrices (no missing values), different subsets of the measured trace elements and isotopes were used in these analyses to allow comparison with the broadest range of potential sources.

In addition to using PLS-DA in a 'single pass' method, the algorithm was used in an iterative mode, in which samples that were completely dissimilar to NSR-F-130509 were eliminated from the comparison data set, the PLS-DA model was recalculated, and then NSR-F-130509 was queried against the new model. The purpose of this iterative approach is to improve the accuracy of the PLS-DA model. Leave-one-out validation experiments conducted by LLNL with over 1700 UOC samples from over 20 sources showed a 50% reduction in misclassifications when PLS-DA was applied iteratively [9]. The reason for this is that the weighting of each of the measured variables in the reduced dimensional classification space is determined by maximizing the ratio of 'between class' to 'within class' variance. Highly dissimilar classes will strongly influence this weighting, producing a space which is very effective at discriminating between these "outlier classes" and everything else. Removing these outlier classes from the model in the first application of PLS-DA ensures that only those variables that are effective at separating the classes which are most similar to the unknown are given a high weighting in the final classification model.

### Results

Initial high resolution gamma-ray spectrometry carried out at both laboratories established that NSR-F-130509 was uranium material of natural isotopic abundance. The absence of isotopes such as  $^{232}U$  and  $^{239}Pu$  above detection limits in LLNL's more detailed results indicated that the sample had not experienced a significant neutron flux (reactor irradiation). Other fission and activation products including  $^{54}Mn$ ,  $^{60}Co$ ,  $^{106}Ru$ ,  $^{125}Sb$ ,  $^{137}Cs$ ,  $^{144}Ce$ ,  $^{152}Eu$  and  $^{182}Ta$ , were also below detection limits.  $^{226}Ra$  was detected at very low levels and was most likely residual from the U ore (incompletely removed during the milling process).

Secondary electron imaging of the seized radioactive material suggested, from the uniformity of the particle morphology, the powder was mostly single phase (i.e. homogeneous). The

irregular to sub-euhedral shaped particles were approximately 0.5-1.0  $\mu\text{m}$  in diameter. The larger particles ( $\sim 10\text{-}100\ \mu\text{m}$ ) observed in the material were agglomerations of these finer particles (Figure 3). Energy dispersive X-ray spectroscopy (EDS) analysis found the material to consist predominantly of uranium and oxygen. As several characteristics of the seized sample matched the UOC from Mary Kathleen Uranium mine (see below), LLNL undertook SEM examination of the Mary Kathleen UOC exemplar as well. The SEM images are shown in Figures 4 and 5. The top two panels in Figure 4 show a comparison of the SEM images for samples prepared simply by surface transfer. Both NSR-F-130509 (on left) and the Mary Kathleen UOC showed a tendency for the smaller grains to agglomerate and the surface morphology of the larger grains was similar, though Mary Kathleen generally exhibited larger agglomerates with rounder shape factors. The bottom two panels of Figure 4 show a comparison of the backscatter electron images for samples that have been disaggregated through ultrasonication in solvent. While disaggregation was observed with both samples, the Mary Kathleen material continued to exhibit generally larger average grain sizes. However, small populations of larger grains, 10–100  $\mu\text{m}$  in caliper diameter, were observed in both samples.

Higher magnification images of the disaggregated samples revealed a difference in the microstructure of smaller grains between NSR-F-130509 and Mary Kathleen (see Figure 5). In particular, the smaller grains in the Mary Kathleen sample (panels on right) displayed rougher, ‘more textured’ morphology while NSR-F-130509 displayed smoother, ‘less textured’ morphology. This difference in microstructure might be evidence of a different processing history between the two materials, for instance changes to the drying conditions of the sample.

The XRD results for the as-received NSR-F-130509 sample and Mary Kathleen UOC are given in Table 2. XRD pattern matching software at both LLNL and ANSTO identified NSR-F-130509 to be predominantly  $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$  with a variety of other minor uranium-bearing phases. LLNL analysis of the Mary Kathleen UOC exemplar identified  $\text{U}_3\text{O}_8$  as the major phase, again with a variety of other minor uranium-bearing phases. The difference in the minor phase composition of the seized sample between ANSTO and LLNL is attributed to slightly differing sample prep and analysis and search-match database differences. The difference in major phase composition between NSR-F-130509 and Mary Kathleen indicated that the two materials had different processing histories.

X-ray fluorescence analysis results indicated that the seized sample was mainly U, with traces of S, Fe and Si. Moisture content determination (to  $140^\circ\text{C}$ ) found that NSR-F-130509 contained  $2.63 \pm 0.05$  wt. % moisture. When heated to  $750^\circ\text{C}$ , a total of  $9.89 \pm 0.08$  wt. % mass was lost. In addition to moisture this was most likely due to loss of sulphate and trace nitrates and organics.

The uranium isotopic abundances determined using ICP-MS for both the seized material and the Mary Kathleen UOC exemplar were consistent with each other and with that of natural uranium (Table 3), confirming the initial gamma spectrometry results. The U assay on the seized sample (dried to  $140^\circ\text{C}$ ) was  $0.7782 \pm 0.0033$  gU/g-sample. The Mary Kathleen UOC sample U assay was  $0.7754 \pm 0.0033$  gU/g-sample. The expected U content based on calculations using the major phase obtained by XRD (ie, if the major phase comprised 100% of the sample) was 0.792 and 0.848 gU/g-sample for NSR-F-130509 and Mary Kathleen UOC, respectively. The reason for the difference between the measured and calculated U content is the presence of minor phases (both crystalline and amorphous).

Model ages for NSR-F-130509 and Mary Kathleen UOC are given in Table 4 (using the  $^{234}\text{U} \rightarrow ^{230}\text{Th}$  system) and were within 3.5 years of each other; 17 January, 1964 ( $\pm 233$  days) for NSR-F-130509 compared with 11 March, 1967 ( $\pm 223$  days) for Mary Kathleen UOC. These model ages estimate the time since last chemical purification of the parent nuclide from the daughter nuclide (assuming complete purification). Incomplete purification will produce ages that are older than the true date of the last chemical purification, and addition or loss of the daughter from the parent nuclide during subsequent processing will result in ages that are either older or younger, respectively, than the true date of purification. LLNL also measured the age of NSR-F-130509 using the  $^{228}\text{Th}/^{232}\text{Th}$  chronometer, but the sample was greater than 40 years old so the isotopic system had reached secular equilibrium.

Table 5 shows the Sr and Pb isotopic results for NSR-F-130509 and for the Mary Kathleen UOC sample. The Pb and Sr isotopic ratios for NSR-F-130509 and the Mary Kathleen samples were highly radiogenic and unique in our experience. The results found in this study were consistent with those reported by Varga et al. for Mary Kathleen UOC [7]. In that study, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for a number of UOCs sourced from 18 other different mines, in 7 different countries, ranged from  $0.70681 \pm 0.00011$  to  $0.73434 \pm 0.00017$ , well below the Mary Kathleen UOC value of  $0.760630 \pm 0.000020$ . Lead isotope ratios ( $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ ) measured on NSR-F-130509 and the Mary Kathleen UOC were very similar and quite different to a range of other UOC samples [7].

The elemental impurity results for NSR-F-130509 and Mary Kathleen UOC are provided in Table 6. In general, the ANSTO and LLNL results were within approximately 20% of each other; larger differences, for example for Ca, Ti, Zn and Cd results, may have been due to either sample inhomogeneity or analytical issues, but this was not investigated further. The approximate levels of impurities were similar for NSR-F-130509 and Mary Kathleen UOC; both samples contained significant concentrations of low mass elements (Na, Mg, Al, K and Ca), Mn, Fe, Zr, light rare earth elements (particularly La and Ce) and Th. These elemental results, together with U and Sr isotopic ratios, were used in the statistical analyses (see below).

Normalised rare earth element patterns have been shown to be valuable in attributing unknown samples of uranium ore and ore concentrates [3, 6]. Figure 6 shows the chondrite-normalized rare earth element concentrations (using ANSTO values) of NSR-F-130509 and UOC and ore obtained from Mary Kathleen along with the UOCs from a number of other Australian mines, both current and formerly operating. The rare earth elemental pattern of NSR-F-130509 was very similar to that of Mary Kathleen (both UOC and ore), while quite distinct from the other samples. The rare earth elemental pattern of Mary Kathleen appears to be unusual, as demonstrated by comparison with 38 UOC samples from 31 mines, from 7 different countries, by Varga et. al. [6].

Ion chromatography analysis found that the only anion present in significant concentrations in the aqueous leachate of the seized sample was sulphate, with both chloride and nitrate present at only trace concentrations. The Mary Kathleen UOC gave similar results (i.e., high sulphate results with only trace amounts of chloride and nitrate) but also contained a trace amount of fluoride. A plot of the ratio of sulphate to chloride measured in the leachates for UOC samples sourced mainly from Australia and Canada is given in Figure 7. Note that the results are presented as ratios, since the particle size of the powders (which influences leach rates) was not standardised prior to leach testing. The presence of a relatively high  $\text{SO}_4^{2-}/\text{Cl}^-$

ratio suggests that  $\text{H}_2\text{SO}_4$  was used in the processing of NSR-F-130509 and chloride was not, similar to the processing of the Mary Kathleen sample (second production phase, see below) [4].

### Uranium sourcing database

By performing principal components analysis (PCA) on the analysis results for NSR-F-130509 together with the UOC analysis results contained in LLNL's uranium sourcing database, and plotting the results against the first two principal components (Figure 8, left), NSR-F-130509 was found to be most similar to the UOC from Mary Kathleen. The loading plots (Figure 8, right) show the influence (both magnitude and direction) of the analytes relative to each principal component axis. Applying partial least squares-discriminant analysis (PLS-DA) iteratively on the same data set confirmed that the sample was most similar to the Mary Kathleen source.

### Associated traditional forensic evidence

Traditional forensic evidence (such as hair, fibres, DNA, and so on) present at a radiological crime scene or nuclear security incident may provide vital clues to link the perpetrator/s with the crime. In this case, potential traditional forensic evidence associated with the seized radioactive powder included the small glass jar which contained the sample (Figure 1) and the label on the jar. The jar was identical to a Kraft Vegemite™ jar. The faded and rusted condition of the lid indicated that the jar was quite old. Kraft manufacturers replaced metal lids with yellow plastic ones in 1991 [14], so the sample has either been in the jar since prior to 1991 or the sample was placed into an old jar. The shape of the Vegemite™ jars was also specific to a given period of time; the clear glass jar in which the sample was found was sold from 1956 to 1991 [14].

The jar was labelled “Gamma Source” with a handwritten (cursive writing), blue bordered, white stick-on label (Figure 1). Possibly, a hand writing expert could help identify a potential criminal (most likely in combination with other intelligence) but this was beyond the scope of the current investigation.

### Discussion

Many analytical characteristics were measured on the seized uranium sample and the major objective of this study (and nuclear forensics in general) was to determine which results were most useful in identifying the sample and its provenance. While some analytical results were unable to be used in this study due to insufficient reference datasets or libraries, which is discussed in more detail below, certain material characteristics allowed a determination with a high degree of confidence, that the source of the seized UOC was Mary Kathleen (or some unknown ore body very like Mary Kathleen). Examination of the normalised rare-earth elemental pattern measured for NSR-F-130509 (Figure 6) indicated a close match with UOC and ore material from Mary Kathleen, while quite distinct from other mines. Both the Sr and Pb isotope ratios measured on NSR-F-130509 were remarkably similar to the UOC from Mary Kathleen, while Mary Kathleen's Sr and Pb isotope ratios are unique based upon our experience with UOC samples. In addition, the high  $\text{SO}_4^{2-}/\text{Cl}^-$  ratios were consistent between NSR-F-130509 and the Mary Kathleen UOC exemplar and strongly suggest that sulphate was used during processing of both materials. Furthermore, multidimensional statistical analysis of the trace elemental and isotopic results from NSR-F-130509, in comparison with results

contained in LLNL's Uranium Sourcing Database, indicated a close match with the UOC from Mary Kathleen when both PCA and iterative PLS-DA was applied. All of these findings strongly suggest that NSR-F-130509 was derived from the Mary Kathleen mine.

Mary Kathleen is an abandoned open cut mine and mill located in northwest Queensland, Australia. It was a metamorphic deposit (total grade 0.13 wt %  $\text{U}_3\text{O}_8$ ; total production 8882 t  $\text{U}_3\text{O}_8$ ) with primary mineralisation uraninite and main gangue the rare earth minerals allanite and stillwellite plus garnet, apatite, amphiboles and feldspars [15]. The mill treated ore from a single pit, i.e., no blending of ore occurred. In 1972, Hartley [16] described Mary Kathleen as the largest mill in Australia. The Mary Kathleen mine/mill had two periods of operation, 1958-1963 and 1976-1982. The milling process during the two periods was different. While both phases used sulphuric acid leaching of the crushed ore, uranium was recovered in the first stage using ion exchange (eluted with  $\text{NaCl}/\text{H}_2\text{SO}_4$ ) and precipitated with magnesia ( $\text{MgO}$ ), while the second stage used solvent extraction ( $(\text{NH}_4)_2\text{SO}_4$  strip) and ammonia ( $\text{NH}_3$ ) precipitation [17, 18].

The age of NSR-F-130509 could be useful in determining whether or not the seized material was derived from one or another of the active periods of the Mary Kathleen mine. However, we must be cautious when interpreting radiochronometric ages of UOC, since we do not know whether the milling process effectively removed the daughter nuclide ( $^{230}\text{Th}$ ) from the raw ore. Indeed, the presence of relatively high Th impurity in NSR-F-130509 and Mary Kathleen UOC ( $5.76 \pm 0.41 \mu\text{g/g-sample}$  and  $4.54 \pm 0.08 \mu\text{g/g-sample}$  respectively, see Table 6) indicated that Th was not completely removed during processing.

The model  $^{234}\text{U} \rightarrow ^{230}\text{Th}$  purification date for NSR-F-130509 was 17 January, 1964 ( $\pm 233$  days), which, given the uncertainty, would overlap with the end of the first operating period. However, we cannot discount the possibility that either the Th was not completely removed in processing or that the UOC was subsequently contaminated with extraneous  $^{230}\text{Th}$ . As mentioned, the milling process during the first period of production involved precipitation of the uranium using magnesia. A comparison of UOC products from the Australian Rum Jungle operation indicates that yellowcakes precipitated using magnesia have  $\sim 0.4\%$  magnesium in the final product (as compared to  $0.03\%$  magnesium when  $\text{NaOH}$  was used for precipitation) [18]. The low level of magnesium in NSR-F-130509 suggested that the magnesia precipitation was not used for this material and, thus, that the material was produced during the second period of production. This would mean that the  $^{234}\text{U}$ - $^{230}\text{Th}$  model age of the seized sample was anomalously old.

The UOC exemplar from Mary Kathleen has a model purification date of 11 March 1967 ( $\pm 223$  days), which corresponds to the period between active production phases. In this case as well, the age is most likely anomalously old. The exemplar from Mary Kathleen was provided with a date of '15/05/77'. The meaning of this date is not known, but, if it represents a production or sampling date, it would again suggest that the material is younger than indicated by the model age and derives from the second period of production (1976-1982). Furthermore, the low level of magnesium in the Mary Kathleen UOC would also indicate that the material derives from the second era of production.

While the elemental and isotopic signatures of NSR-F-130509 point to Mary Kathleen as the most likely source of the seized material, differences in the XRD results and the SEM microstructure analysis might suggest otherwise. However, these differences are probably due to differences in the processing conditions used to produce the UOC, most likely related

to drying temperature and/or time. It is known that different processing conditions can lead to dissimilar particulate morphologies [19]. Given that the major phase measured in the seized sample ( $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ ) was different to that measured in the Mary Kathleen UOC exemplar ( $\text{U}_3\text{O}_8$ ), we should expect some differences in the processes used to produce them. It is reasonable to expect such changes to have taken place during the 6 years of operation of the second phase of production (1976-1982).

### **Future Work**

Several analytical techniques were employed to characterise the seized sample but were not reported here as further research is required to understand and interpret the results and obtain data from known material for development of a database or library. For instance, organic analysis of NSR-F-130509 was carried out using solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) to look for the presence or absence of any organic compound used in Mary Kathleen processing, such as polyacrylamide flocculant known to have been used during processing [18] or alamine-336 used as extractant for solvent extraction [17]. Near-infrared (NIR) diffuse reflectance spectroscopy (DRS) is also a powerful, non-destructive analytical technique that can provide chemical information about samples without sample preparation. Initial test-work has indicated that the chemical information measured in the NIR spectra may help identify process techniques (e.g., the NH band intensity in ammonium diuranate samples) as well as source location (e.g., the OH bands). This technique may also give a non-subjective measure of colour, which can be a useful signature.

Stable isotope (C, S, N and O) analysis may also prove useful in future cases of unknown UOC once a larger body of data is available for comparison. The oxygen isotopic compositions of uranium ore concentrates are affected by the oxygen isotopic composition of the uranium ore and the chemicals and water used to process the ore into ore concentrate, as well as by the process itself, which may cause isotopic fractionation. LLNL is in the early stages of developing a database and interpretive methodology for oxygen isotopic compositions of uranium ores and ore concentrates.

From IDMS analyses by MC-ICPMS, one can obtain the Th concentration in the sample and the  $^{230}\text{Th}/^{232}\text{Th}$  ratio. For natural UOCs, this ratio may be useful in identifying the source of the U ore, but only with a suitable database. Development of this database is also an area for future work.

Another potential signature for UOCs is the Pu content. In this study, Pu was analysed by MC-ICPMS following radiochemical separation. The Pu may be fallout from atmospheric weapons testing or  $^{239}\text{Pu}$  may be produced naturally via neutron capture on  $^{238}\text{U}$  in the ore. The radionuclide  $^{236}\text{U}$ , produced via neutron capture on  $^{235}\text{U}$ , is also a potential geographic indicator.

In addition to these chemical signatures, we need to understand whether morphological/microstructural differences, such as those seen here between NSR-F-130509 and the Mary Kathleen exemplar, are significant or not. A study examining quantitative variations in particle size, aspect ratio and other physical attributes on a day-to-day basis of samples derived from a single production process operating on a single feed-stream would be useful in understanding the true significance of these differences.

### **Conclusion**

Chemical and isotopic measurements indicate that the radioactive powder material provided to ANSTO by an Australian state policing agency was a natural uranium ore concentrate (UOC). Sr and Pb isotopic results and elemental analyses (particularly the REE pattern), coupled with detailed statistical analysis, strongly suggested that the seized sample was derived from the Mary Kathleen mine during its second production period. The age of the material and its anion composition support this conclusion. The slightly different phase composition and microstructural analysis between the seized powder and an exemplar of UOC from Mary Kathleen suggest that the two samples could have slightly different processing histories, most likely different drying temperatures and/or times.

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Table 1. Summary of characterisation techniques used to examine the seized uranium material (and UOC from Mary Kathleen (MK) Uranium mine).

Analytical Technique	Measured Parameter
High resolution gamma-ray spectrometry	Initial categorization, approximate uranium isotopic abundance, activation and fission products
Optical microscopy	Physical characterisation – particle size and morphology
Electron microscopy (SEM/EDS)	Particle size; Microstructure and elemental composition
XRD	Phase composition
XRF	Elemental composition (high content impurities)
Vis/NIR reflectance spectroscopy	Chemical information with no sample preparation; colour, CH, OH and NH bonds
Solid-phase microextraction (SPME) and GC-MS	Volatile and semi-volatile organic compounds
Loss-on-heating	Moisture content (to 140 °C for 2 hours) and content of thermally removed species (to 750°C for 12 hours)
MC-ICP-MS (plus chemical separation)	U assay and isotopic analysis Age determination and Sr and Pb isotopic analysis
ICP-MS	Elemental impurities (including REEs)
Neutron activation analysis (NAA)	Elemental impurities in MK ore sample
Ion chromatography	Anions ( $F^-$ , $Cl^-$ , $Br^-$ , $NO_3^-$ , $SO_4^{2-}$ , $PO_4^{3-}$ )
Elemental analyser	Stable isotopes of C, N, O and S

Table 2. X-Ray Diffraction results for the seized sample and Mary Kathleen UOC

Sample	Major Phase	Minor Phases
NSR-F-130509 (ANSTO)	$UO_3 \cdot 0.8H_2O$	$Na_2(UO_2) \cdot 6H_2O$ , $UO_3$ , $UO_2$
NSR-F-130509 (LLNL)	$UO_3 \cdot 0.8H_2O$	$(UO_2)_4O(OH)_6(H_2O)_5$ , $U_3O_8$ ,
Mary Kathleen (LLNL)	$U_3O_8$	$(UO_2)_3(PO_4)_2 \cdot 4H_2O$ , $SiO_2$ , $FeS$ , $CuSiO_3 \cdot 2H_2O$ , $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$

Table 3. Uranium isotope ratios determined by MC-ICP-MS analysis (with expanded uncertainties, k=3)

Sample ID	$^{234}\text{U}/^{238}\text{U}$	Uncertainty	$^{235}\text{U}/^{238}\text{U}$	Uncertainty	$^{236}\text{U}/^{238}\text{U}$	Uncertainty
NSR-F-130509	0.00005485	0.00000033	0.007250	0.000015	6.9E-09	5.7E-09
Mary Kathleen UOC	0.00005482	0.00000032	0.007250	0.000012	< 1E-8	

Table 4. Model ages calculated from  $^{230}\text{Th}$  and  $^{234}\text{U}$  concentrations (with expanded uncertainties, k=3)

Sample	Reference Date (i.e., date sample analysed)	Model Age (years) (i.e., years before reference date)	Uncertainty	Model Date	Uncertainty (days)
NSR-F-130509	28 Jan. 2011	47.03	0.64	17 Jan. 1964	233
Mary Kathleen UOC	14 Mar. 2011	44.01	0.61	11 Mar. 1967	223

Table 5. Sr and Pb isotope ratios measured using TIMS (for Sr) and MC-ICPMS (for Pb) (with expanded uncertainties)

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
NSR-F-130509	0.757233 ( $\pm 0.000015$ )	53.385 ( $\pm 0.082$ )	50.995 ( $\pm 0.080$ )	392.050 ( $\pm 0.610$ )	0.136 ( $\pm 0.001$ )	0.130 ( $\pm 0.001$ )
Mary Kathleen UOC	0.761020 ( $\pm 0.000012$ )	48.671 ( $\pm 0.024$ )	38.158 ( $\pm 0.019$ )	255.95 ( $\pm 0.12$ )	0.190154 ( $\pm 0.000018$ )	0.149085 ( $\pm 0.000011$ )
Mary Kathleen UOC <sup>a</sup>	0.760630 ( $\pm 0.000020$ )	48 <sup>b</sup>	40 <sup>b</sup>	275 <sup>b</sup>		0.1479 ( $\pm 0.0023$ )

<sup>a</sup>Values taken from Varga et al., 2009 [7], <sup>b</sup>Values read off graph

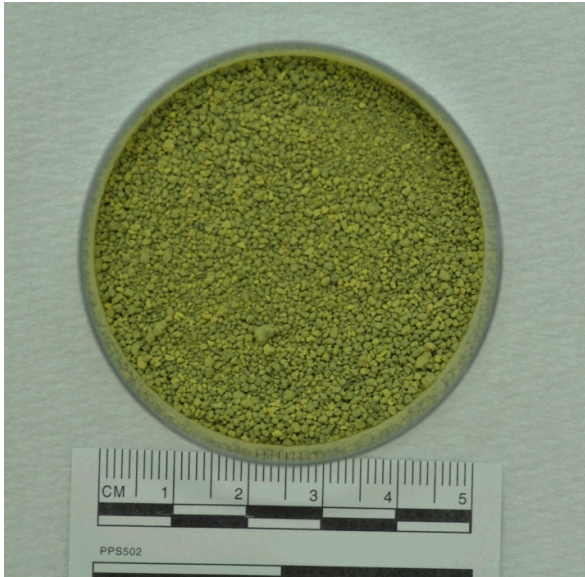
Table 6. Results of ICP-MS trace impurity analysis. Concentrations are in  $\mu\text{g/g}$  of sample (as received, not dried), along with GUM compliant uncertainties.

Element	NSR-F-130509 (ANSTO)	NSR-F-130509 (LLNL)	Mary Kathleen UOC (LLNL)
Na	< 100	78 $\pm$ 3	62 $\pm$ 5
Mg	17 $\pm$ 0.6	16.2 $\pm$ 0.6	14.5 $\pm$ 1.5
Al	< 100	82 $\pm$ 20	47.5 $\pm$ 1.1
K	13 $\pm$ 1	< 100	< 100
Ca	102 $\pm$ 15	213 $\pm$ 18	160 $\pm$ 9
Sc	0.1 $\pm$ 0.05	nm	nm
Ti	6.8 $\pm$ 1.8	2.4 $\pm$ 0.4	1.77 $\pm$ 0.08
V	0.1 $\pm$ 0.02	< 0.1	0.1 $\pm$ 0.02
Cr	0.5 $\pm$ 0.2	< 0.1	< 0.4
Mn	103 $\pm$ 15	79.6 $\pm$ 0.7	24.67 $\pm$ 0.15
Fe	419 $\pm$ 65	320 $\pm$ 50	290 $\pm$ 50
Co	0.3 $\pm$ 0.01	0.25 $\pm$ 0.06	0.1065 $\pm$ 0.0014
Ni	0.5 $\pm$ 0.2	< 1	< 1
Cu	0.6 $\pm$ 0.08	< 0.4	< 0.3
Zn	4.7 $\pm$ 0.3	6.9 $\pm$ 0.3	7.4 $\pm$ 1.9
Ga	0.3 $\pm$ 0.02	< 0.2	< 0.2
Ge	0.2 $\pm$ 0.05	< 0.2	< 0.2
As	1 $\pm$ 0.16	< 0.6	0.22 $\pm$ 0.08
Se	< 0.1	< 0.05	< 0.3
Rb	0.2 $\pm$ 0.02	0.22 $\pm$ 0.05	0.137 $\pm$ 0.017
Sr	1.6 $\pm$ 0.1	1.3 $\pm$ 0.1	0.87 $\pm$ 0.09
Y	0.2 $\pm$ 0.02	0.15 $\pm$ 0.03	0.085 $\pm$ 0.004
Zr	574 $\pm$ 88	439 $\pm$ 3	249 $\pm$ 5
Nb	0.1 $\pm$ 0.01	< 0.003	< 0.003
Mo	3.9 $\pm$ 0.72	2.79 $\pm$ 0.12	3.43 $\pm$ 0.14
Ru	< 0.05	< 0.02	< 0.02
Rh	nm	< 0.001	< 0.001
Pd	< 0.05	< 0.015	< 0.015
Ag	3 $\pm$ 0.05	< 1	0.494 $\pm$ 0.019
Cd	0.6 $\pm$ 0.03	0.3 $\pm$ 0.07	0.1638 $\pm$ 0.0005
Sn	0.3 $\pm$ 0.22	< 5	< 0.05
Sb	< 0.05	< 0.05	< 0.05
Te	nm	< 0.2	< 0.2
Cs	1.7 $\pm$ 0.6	< 0.4	0.14 $\pm$ 0.06
Ba	7.6 $\pm$ 0.51	6.6 $\pm$ 0.4	9 $\pm$ 11
La	29 $\pm$ 3.3	20.9 $\pm$ 0.4	13.73 $\pm$ 0.07
Ce	48 $\pm$ 0.4	34 $\pm$ 0.3	22.08 $\pm$ 0.13
Pr	4.1 $\pm$ 0.54	2.89 $\pm$ 0.15	1.775 $\pm$ 0.016
Nd	10 $\pm$ 1.3	7.1 $\pm$ 0.2	4.201 $\pm$ 0.012
Sm	0.6 $\pm$ 0.12	0.41 $\pm$ 0.05	0.266 $\pm$ 0.012
Eu	0.1 $\pm$ 0.02	< 0.04	0.025 $\pm$ 0.005
Gd	0.9 $\pm$ 0.15	0.53 $\pm$ 0.06	0.311 $\pm$ 0.014
Tb	0.04 $\pm$ 0.01	< 0.02	0.0141 $\pm$ 0.0008
Dy	0.1 $\pm$ 0.01	< 0.04	0.027 $\pm$ 0.001
Ho	< 0.01	< 0.01	0.0039 $\pm$ 0.0003
Er	< 0.05	< 0.01	0.0082 $\pm$ 0.0008
Tm	< 0.01	< 0.002	< 0.002

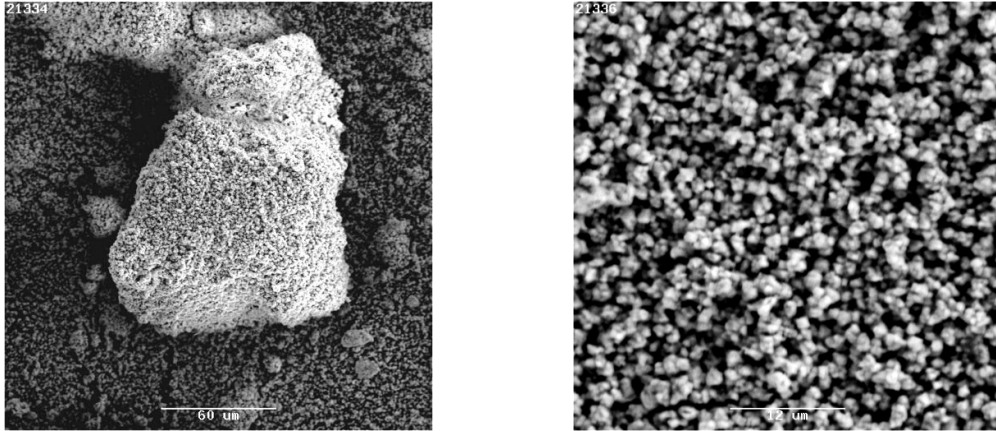
Yb	< 0.02	< 0.01	0.006 ± 0.003
Lu	< 0.01	< 0.001	< 0.001
Hf	0.4 ± 0.12	0.13 ± 0.04	0.049 ± 0.007
Ta	nm	< 0.002	< 0.002
W	2.9 ± 0.23	1.78 ± 0.08	2.244 ± 0.018
Re	< 0.01	< 0.01	< 0.01
Ir	nm	< 0.005	< 0.005
Pt	< 0.01	< 0.005	< 0.005
Tl	< 0.01	< 0.01	< 0.01
Pb	3.9 ± 0.5	6.3 ± 0.4	1.29 ± 0.08
Th	5.76 ± 0.41	7.03 ± 0.18	4.54 ± 0.08



*Figure 1. Glass jar labelled “Gamma Source” containing radioactive material received by ANSTO.*



*Figure 2. Green coloured radioactive material designated NSR-F-130509.*



*Figure 3. Secondary electron images of a larger particle (left) and the same cluster at higher magnification (right) showing the particulate morphology of the seized material.*



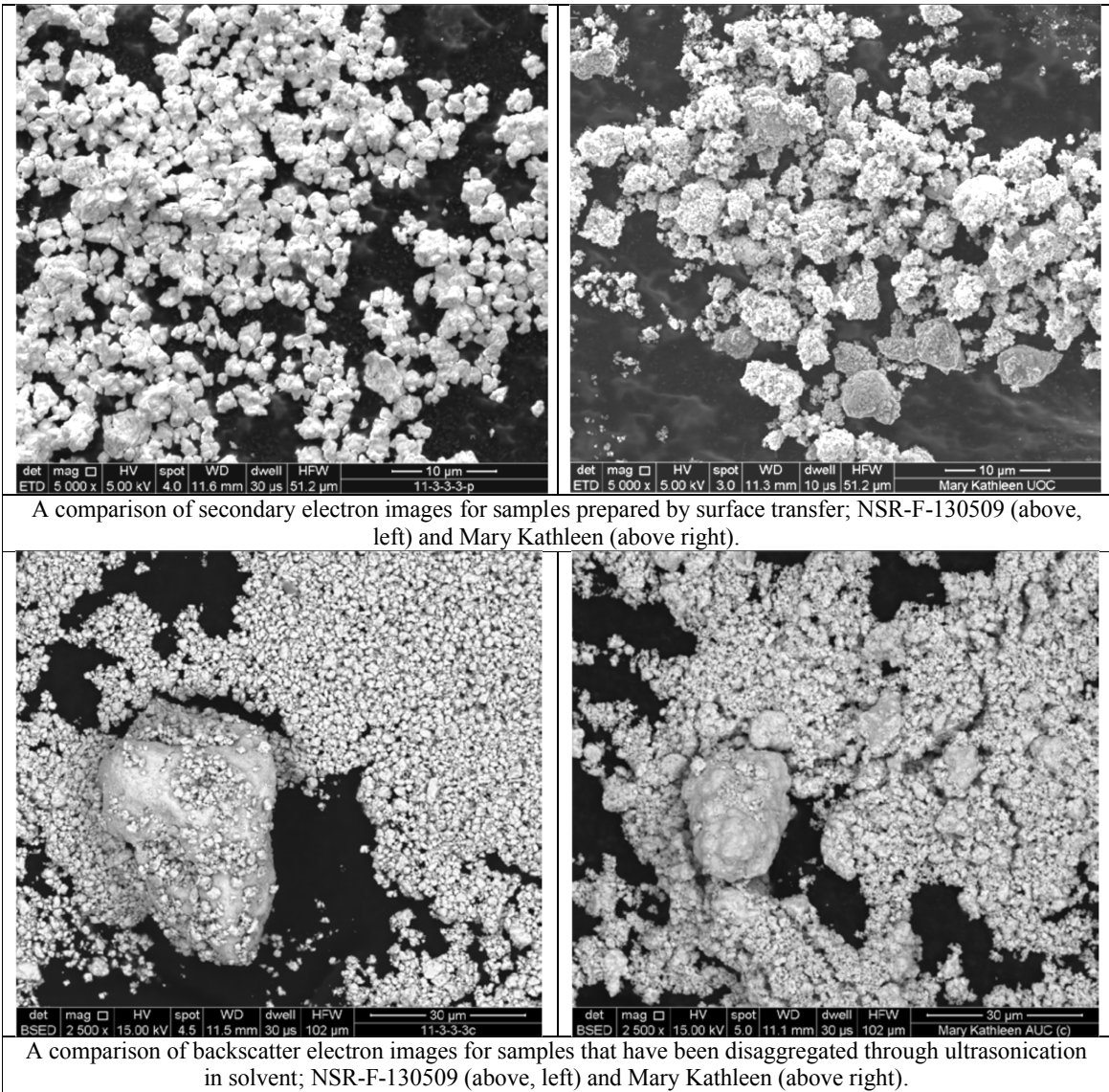
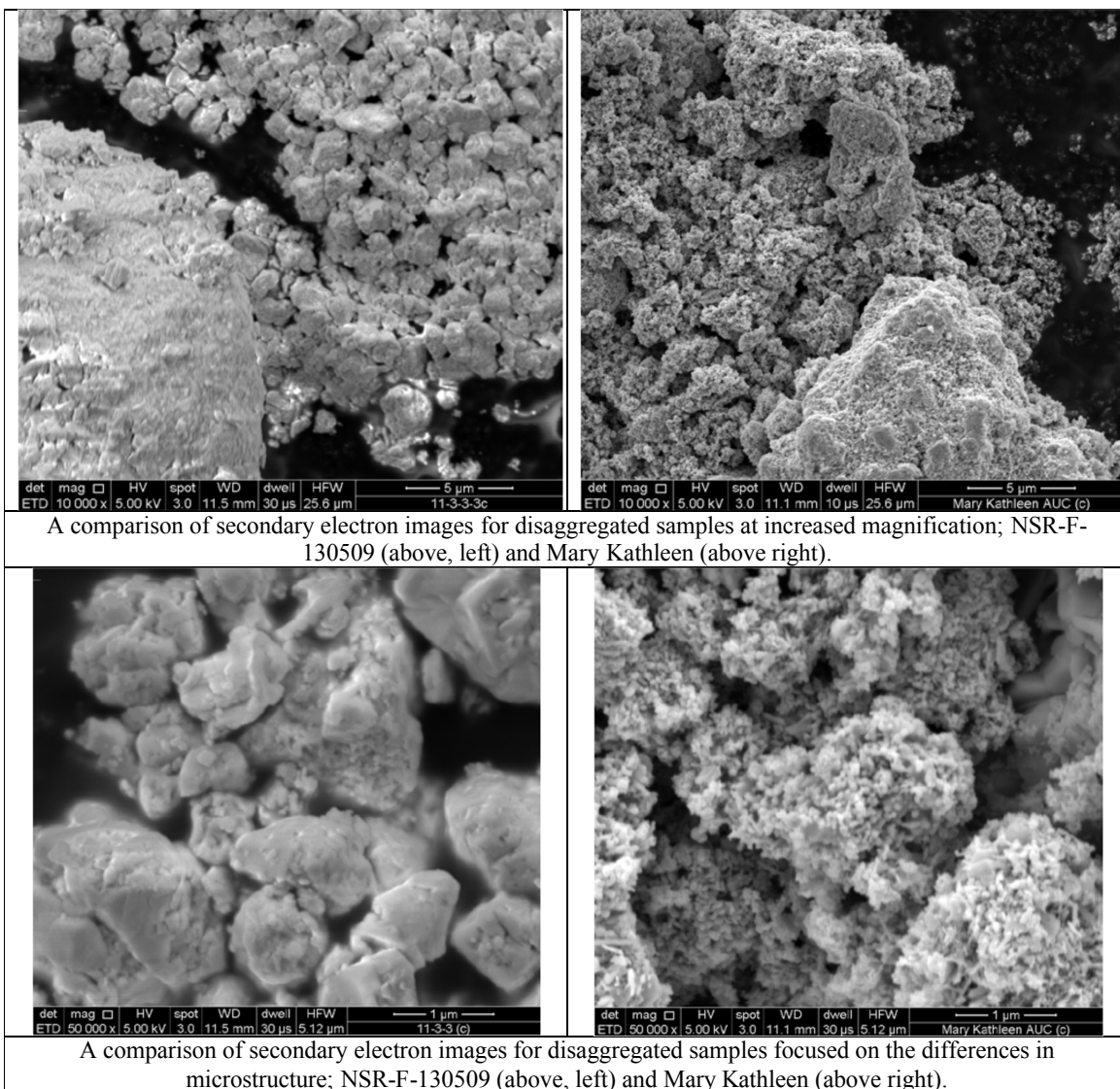


Figure 4. Secondary electron images of the seized sample compared with Mary Kathleen UOC (NSR-F-130509 on left and Mary Kathleen on right) prepared by surface transfer (top) and ultrasonication (bottom). Scale bar for the top images is 10 µm and 30 µm for the bottom images.



*Figure 5. A comparison of secondary electron images for disaggregated samples of NSR-F-130509 (on left) and Mary Kathleen (on right,) at increased magnification. Scale bar for the top images is 5  $\mu$ m and 1  $\mu$ m for the bottom images.*

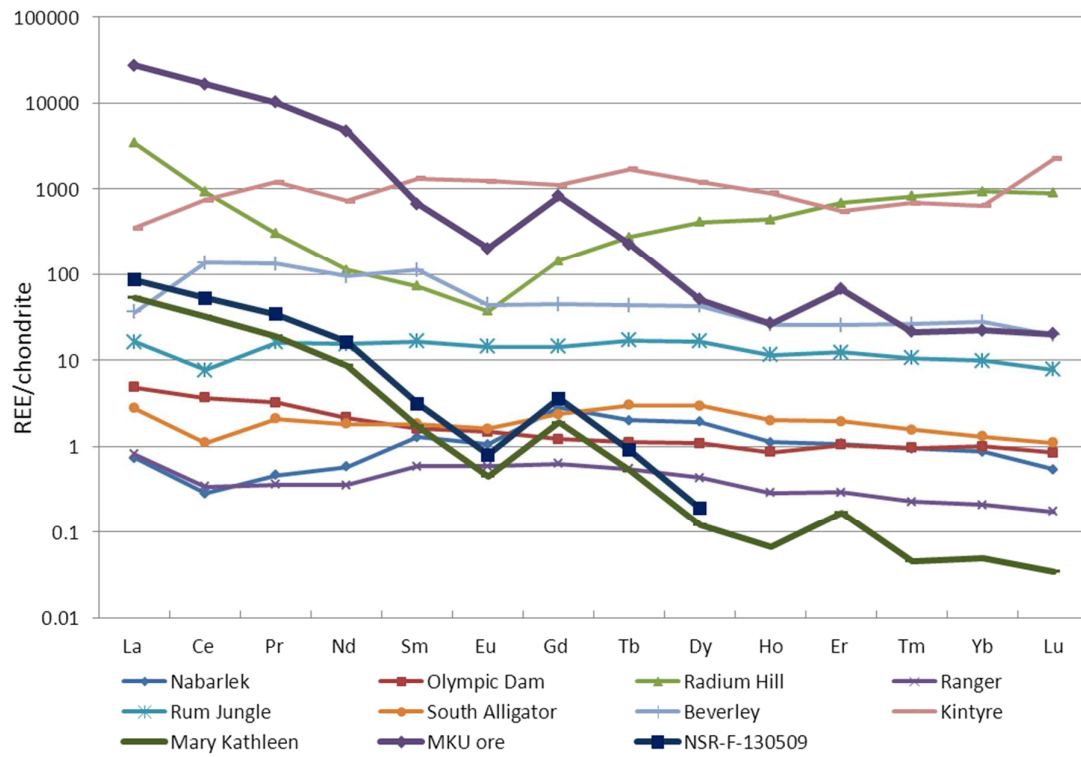


Figure 6 Chondrite normalised rare earth element (REE) plot for Australian UOC samples and also Mary Kathleen Uranium (MKU) ore.

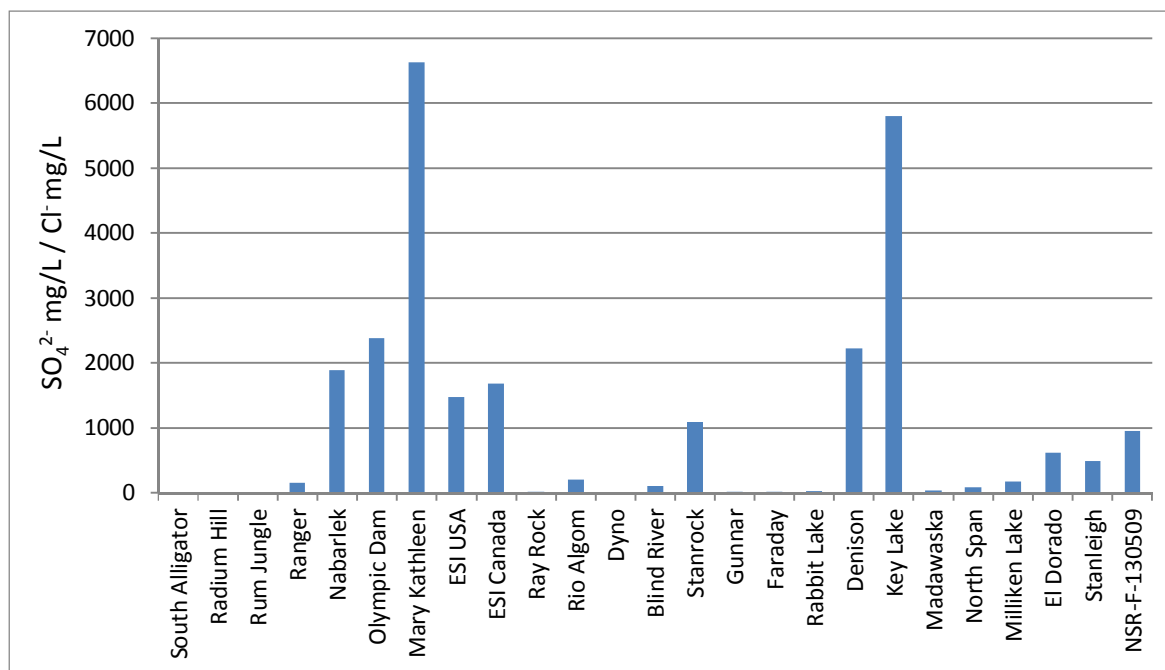


Figure 7. Sulphate/Cl<sup>-</sup> ratios measured in the aqueous leachate of a range of UOC samples including Mary Kathleen and NSR-F-130509

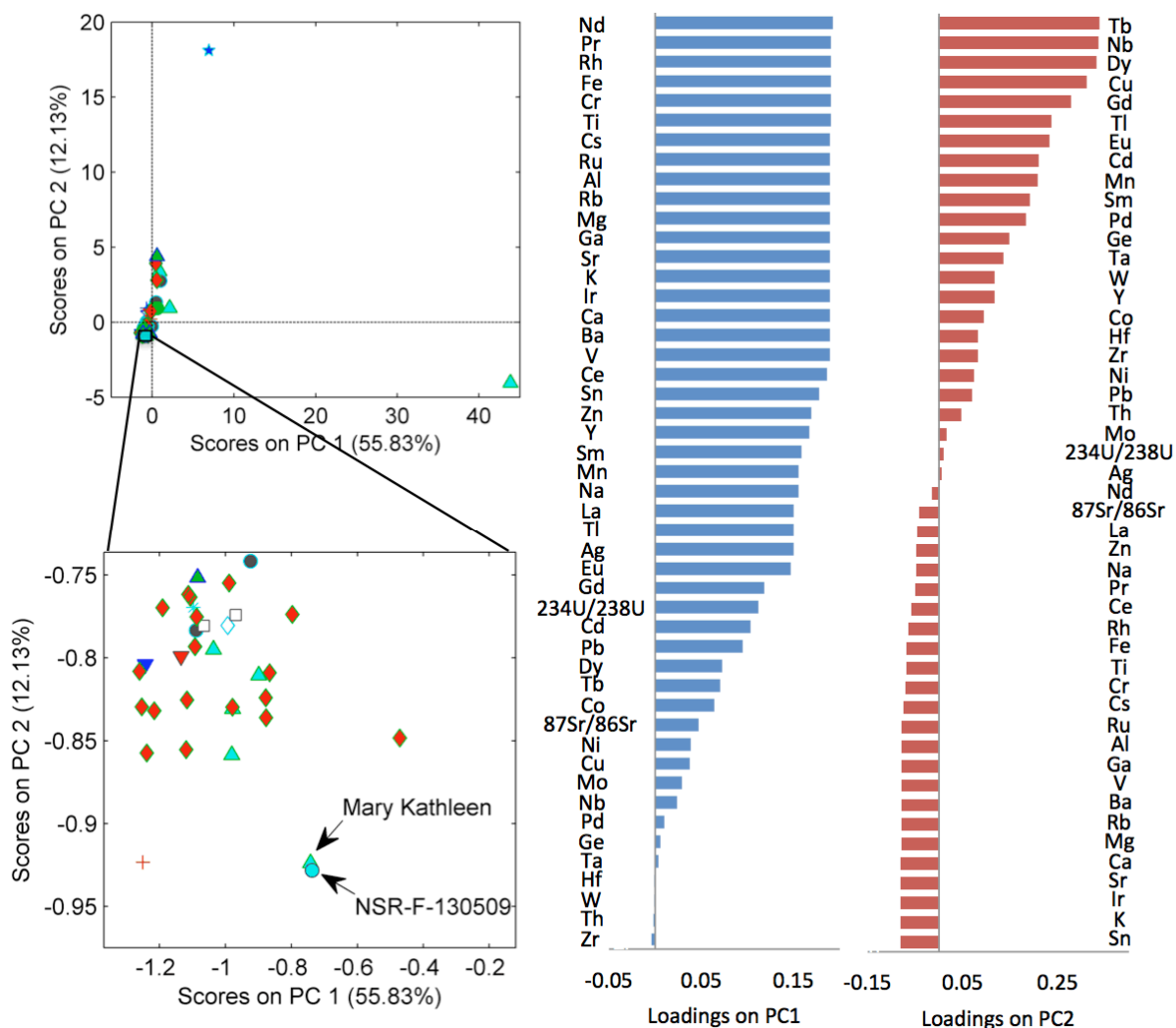


Figure 8. Principal Components Analysis (PCA) of a UOC dataset along with NSR-F-130509. The scores plots (left) show the mapping of 77 different samples representing 76 different production sources into the PCA space. Symbols indicate production countries. The bar plots (right) show the loadings (i.e., the weighting) for each of the 48 analytes on the two PCs.